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Influence of structural defects on the viscoelastic properties of a lamellar lyotropic phase

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Résumé. Nous avons mesuré les modules de compressibilité et de divergence ainsi que la mobilité des dislocations dans la phase lamellaire du système C_{12}E_5-H_2O. Le module de compressibilité a une valeur classique (2,5 \times 10^7 \text{ dyn/cm}^2) alors que le module de divergence est petit (6 \times 10^{-8} \text{ dyn}) et que la mobilité est élevée (6 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1} \text{ g}^{-1}). Cette dernière donnée sert à calculer le coefficient de perméation. Ces valeurs sont ensuite discutées en relation étroite avec la présence de défauts révélés par des études antérieures [11].

Abstract. We measured compressibility and splay elastic moduli, and the mobility of dislocations of the lamellar phase of C_{12}E_5-H_2O system. The compressibility modulus has a usual value (2.5 \times 10^7 \text{ dyn/cm}^2) while the splay modulus is small (6 \times 10^{-8} \text{ dyn}) and the mobility is high (6 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1} \text{ g}^{-1}). These results are used to calculate the permeation coefficient. These values are then discussed with respect to the presence of defects, revealed by former studies [11].

1. Introduction.

Lamellar lyotropic phases are often very viscous, hence it is difficult to orient samples. This is one reason why there are very few available experimental data on viscoelastic properties of these systems, because measurements require perfectly oriented samples. Most studies were carried out on phospholipidic lamellar phases, for obvious biological interests. Obtaining oriented samples is a real difficulty. This is emphasized by a paper of L. Powers and N. A. Clark where a value of $\lambda$ \(^{(1)}\) is given, entitled « Preparation of large monodomain phospholipid bilayer smectic crystals » [1]. J. P. Lepesant et al. have measured on the same systems sound velocities by Brillouin light scattering experiments, and deduced elastic moduli [2]. Servuss et al. have measured splay modulus of lecithin bilayers building giant vesicles [3]. W. K. Chan and W. W. Webb observed the dynamic behaviour and the annihilation of edge dislocations with fluorescence experiments [4]. They obtained the permeation coefficient [5] of lamellar phase of lecithin in aqueous solution.

Recently, new examples of lamellar phases, with low effective viscosity, were found to be easily oriented between glass plates. Their common feature is that they are rich in thermodynamically stable defects such as pores, channels, etc [6] which are called structural defects, in contrast with textural defects such as focal domains which can anneal with an adequate thermomechanical treatment.

We studied samples of lamellar phase of a non-ionic surfactant in aqueous solution (73 % of C_{12}E_5 in weight, pentaethylene glycol dodecyl ether, in water). The phase diagram, recalled from reference [7] is shown in figure 1. The isotropic high temperature phase has an inverse structure. Between the lamellar phase and the isotropic phase exists a very tiny domain of nematic phase which is not pictured in figure 1 and has been revealed very recently [8].

\[^{(1)}\] $\lambda = (K/B)^{1/2}$ with $K$ splay modulus and $B$ compressibility modulus.
Spin labelling experiments on the lamellar phase have revealed the presence of highly curved regions \((R = 1.5 \text{ nm})\), whose concentration increases with temperature very abruptly when approaching the transition [9]. An electron microscopy study on replicas of freeze fractured samples has shown that part of the curvature is due to the core of dislocation loops, which cross layers, and built with pieces of screw and edge dislocations. However, other sources of curvature, such as microscopic pores, may also exist at the same time [10].

In this article we shall describe the viscoelastic behaviour when dilating and compressing a homeotropic sample perpendicularly to the layers. We first describe the experimental system, then we present a few experiments which give us the compressibility and the splay elastic moduli as well as the mobility of edge dislocations. These results are used to calculate the permeation coefficient which is involved in the low effective viscosity which we observed. The value of this coefficient is discussed with respect to the presence of defects as those revealed by ESR experiments and electron microscopy studies [11].

2. Experimental part.

Samples can be either compressed or dilated perpendicularly to the layers, either in a continuous way with controlled speed or abruptly with controlled amplitude.

2.1 Apparatus. — The sample is deformed by three stacks of piezoelectric ceramics through a rigid frame. The apparatus is symbolically represented in figure 2. Let \(k\) be the elastic modulus of the cell framework. Testing leads to \(k = 5 \times 10^3\) cgs. \(u(t)\) and \(a(t)\) are the displacements of the ceramics and that of the sample, respectively. These data are recorded simultaneously as a function of time, with a 5 nm resolution. Any further description of the apparatus can be found in [12].

2.2 Sample preparation. — Samples are prepared between two circular glass plates, polished to \(\lambda\) and coated with polysilane. Plates make a small known angle \(\alpha\) between them. Slow cooling of the sample from the isotropic high temperature phase leads to perfectly homeotropic lamellar samples. In an ideal case, this geometry leads to a grain boundary in the middle of the sample, built with edge dislocations to release the thickness variation due to the angle between the plates. A cylindrical seal slightly compressed, ensures tightness and does not perturb the behaviour of the cell owing to its adequate flexibility (see Fig. 3). The thickness of each sample is 100 \(\mu\)m. After each run, the sample is carefully and slowly brought back to its previous thickness. Experiments showed that a new test can be performed after a few minutes of annealing at test temperature. Numerous tests have shown that samples lose less than 1 % of water when heated one hour at 80 °C.
3. Determination of compressibility modulus $B$ and of mobility of edge dislocations, $m$. Compression experiments.

3.1 Principles of Measurements. — To measure the compressibility modulus and the mobility of edge dislocations, one imposes a voltage step to the ceramics. The compressed sample is deformed, first in an elastic way (« instantaneous » elastic response $a_0$ which is actually the response at 50 ms, due to limit of our recorder) and then in a plastic way by climb of edge dislocations. Let $\rho_m$ be the density of mobile dislocations, assumed to remain constant during the experiment. A simple calculation leads to an exponential relaxation law [12]:

$$a(t) = u_0 \left( 1 - c \exp \left( -\frac{t}{\tau^*} \right) \right) \quad (1a)$$

with

$$a_0 = u_0 (1 - c) \quad \text{and} \quad c = \left( 1 + \frac{kd}{B} \right)^{-1} \quad (1b)$$

$$\tau^* = \tau \left( 1 + \frac{B}{kd} \right), \quad \tau = (\rho_m b m B)^{-1} \quad (1c)$$

where $d$ is the thickness of the sample, and $b$ is the Burgers vector of an edge dislocation. Knowing $\rho_m$ (this point will be discussed further), the measurement of $a_0$ and of the relaxation time $\tau^*$ yields $B$ and $m$.

3.2 Experimental Results. — Imposed deformation $a_0$ lays between 5 nm and 50 nm (i.e. 1 to 10 layer thickness). The reproducibility of our results is equal to $\pm 20\%$ if working quickly (within two hours), to avoid consequences of drying (see Fig. 1).

Figure 4.1 shows a typical relaxation curve. Formulae (1) describe well the general features of the curve. We can check that curve of instantaneous deformation $u_0 = f(a_0)$ (see Fig. 5) is a line passing through the origin which reveals an elastic behaviour. Measuring the slope, we can calculate $B$ from formula (1b). A few values are given in table I. The mean value is equal to $2.5 \times 10^7$ dyn/cm$^2$. A range of experiments on a given sample shows that $B$ does not vary much with temperature (see Fig. 6).

On each relaxation curve we also measured a characteristic time. It does not vary with the amplitude of deformation, except for a slight decrease at high compressions. Values given in table I are related to small deformations. Relaxation time varies as $1/\alpha$, where $\alpha$ is the angle between the plates. This means that mobile dislocations responsible for the plastic behaviour belong mainly to the grain boundary located in the middle of the sample. It shows that dislocation loops, which cross layers, revealed by former studies do not take part, to first approximation, in the plastic behaviour. This point is discussed in the appendix. According to this remark we can calculate $\rho_m$:

$$\rho_m = \frac{\alpha}{bd} \quad (2)$$
Table I. — Each line is related to one sample characterized by the angle $\alpha$ between the plates. All measurements given in this table have been performed at 50 °C. We recall $\tau = d/mB\alpha$ and $\lambda = (K/B)^{1/2}$ with $d$, thickness of a sample, equal to 100 μm.

<table>
<thead>
<tr>
<th>$\alpha$ (rd)</th>
<th>$B$ (erg/cm³)</th>
<th>$\tau$ (s)</th>
<th>$m$ (cm² s⁻¹)</th>
<th>$\lambda$ step dil. exp. (nm)</th>
<th>$\lambda$ ct. speed exp. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5 \times 10^{-4}$</td>
<td>$3 \times 10^{7}$</td>
<td>1.5</td>
<td>$4 \times 10^{-7}$</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>$2.5 \times 10^{7}$</td>
<td>0.6</td>
<td>$7 \times 10^{-7}$</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>$3 \times 10^{-3}$</td>
<td>$2 \times 10^{7}$</td>
<td>0.2</td>
<td>$8 \times 10^{-7}$</td>
<td>0.5</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Fig. 6. — Compressibility modulus $B$, versus temperature. Set of points obtained from measurements on the same sample. Errors on the angle and on the thickness of the sample are constant so the conclusions on the variation of $B$ are valid though the error on the absolute value of $B$ is $10^7$ dyn/cm². Error bars take into account only errors on deformation measurements.

and then deduce $m$, knowing $\tau$ and $B$ (values in Table I). The mean value of $m$ at 50 °C, for the three samples which we already mentioned, is $m = 6 \times 10^{-7}$ cgs. In figure 7, the mobility is plotted against temperature. It yields an activation energy estimated at $\approx 0.4$ eV.


4.1 Principles of Measurements. — To measure $K$, one can use two methods. Both depend on the existence of the undulation instability of layers above a critical dilation $a_0^c$ given by [13]:

$$a_0^c = 2 \pi \lambda$$

(3)

where $\lambda = (K/B)^{1/2}$ is a characteristic length of the lamellar phase.

In the first method, the sample is dilated abruptly. In the following this is called « a step dilation » experiment. Previous experiments on thermotropic smectic A have revealed a strong anelastic behaviour above the threshold [14, 15]. It is characterized by an abrupt increase of $a_0$, and is easy to observe experimentally. That way, we can deduce the value of the threshold $a_0^c$ and then calculate $\lambda$ and $K$, knowing $B$.

In the second method, the sample is dilated at constant speed. Above a critical speed $v_c$ the undulation of layers occurs [16]. Assuming that concentration of mobile dislocations remains constant during the experiment, one can then calculate:

$$v_c = 2 \pi \rho_m bm/(KB)^{1/2}$$

(4)

then

$$v_c \tau = 2 \pi \lambda.$$ 

(5)

This product has the noticeable feature of being independent of $\rho_m$. It yields directly $\lambda$. $\tau$ is the relaxation time given by formula (1c) and measured with compression experiments.

4.2 Experimental Results. — We shall first give the results obtained with the step dilation method. As previously, each relaxation curve can be characterized by an instantaneous response $a_0$, which is followed by a slow relaxation (see Fig. 4.2). Yet one can notice important differences with compression experiments:

i) Instantaneous deformation curve, $u_0 = f(a_0)$ is
still a line but it does not pass any longer through the origin (see Fig. 5). This means that the sample has an anelastic behaviour.

ii) When the lattice of focal parabolae [17] occurs, the slope of the line changes (see Fig. 5 and Fig. 8).

iii) The slow relaxation part of the curve is no longer exponential as we described it with a simple model in the former paragraph.

These differences do characterize the non-linear regime of layer undulations, whose threshold lays at very low deformations, unfortunately, beyond our experimental reach. In order to estimate the threshold we extrapolate the line \( u_0 = f(a_0) \) towards small deformations. Its intersection with the line \( u_0 = f(a_0) \) for compression experiments (Fig. 5) gives a value for \( a_0 \) which we identify with \( a_0 \). This method, which depends upon the assumption of a non-elastic behaviour just at the undulation occurrence [14] yields \( \lambda \) equal to 0.5 nm, as calculated from formula (5) (see Table I).

We shall now give the results of the « constant speed dilation » method. At low speed the sample remains homeotropic during the deformation whose total amplitude is equal to 10 μm. Above a threshold value \( v_e \) estimated with an accuracy of 20 % for each sample, a lattice of focal parabolae arises, its optical contrast quickly increasing as dilation goes on. This lattice is exactly the same as the one obtained with a step dilation of high amplitude (see Fig. 8).

From experiments on thermotropic smectics, one knows that under growing dilation, layer undulation develops and blocks edge dislocations [18] and then leads rapidly to layer breaking and to the nucleation of a lattice of parabolae. This remark tells that we can identify the measured critical speed and the critical value calculated in the previous paragraph. From the numerical values of \( \tau \) and \( v_e \) given in table I, we calculate a mean value of \( \lambda \) from formula (5). It yields \( \lambda \approx 0.5 \) nm, which is consistent with our former determination (Table I). From \( B \), we then deduce \( K \).

We obtain \( K = 6 \times 10^{-8} \). Within the accuracy of our method (± 50 %), \( K \) does not vary with temperature.

4.3 SUMMARY OF THE RESULTS. — For samples at 50 °C we found:

- compressibility modulus \( B = 2.5 \times 10^7 \) dyn/cm²
- splay modulus \( K = 6 \times 10^{-8} \) dyn
- mobility of edge dislocation \( m = 6 \times 10^{-7} \) cm² sg⁻¹.

We comment on these figures in the next paragraph.

5. Discussion.

The value of \( B \) is the same as what has been found for thermotropic smectics [19], but smaller by 2 orders of magnitude than that measured in a phospholipidic smectic [2].

On the other hand, the value found for \( K \) is smaller than values obtained for thermotropic smectics and for bilayers in giant vesicles [3] (where \( K \) is given equal to \( 10^{-5} \) dyn.) This high flexibility of the interface is consistent with the existence of highly curved defects as revealed by former studies.

But the most surprising result is the value of the mobility of dislocations, which is much larger than that obtained by W. K. Chan and W. W. Webb [4] (\( m = 10^{-15} \) cm² sg⁻¹) with a phospholipidic lamellar system, and quite similar to that measured on a thermotropic smectic (8CB) [20].

The Orsay Liquid Crystal Group has shown that mobility is directly related to the permeation coefficient \( \lambda_p \) [21]:

\[
m = (\lambda_p / \mu)^{1/2},
\]

where \( \mu \) is the shear viscosity « parallel to the layers » and assumed equal to 0.1 poise. We thus obtain \( \lambda_p = 4 \times 10^{-14} \) cm² poise, as compared to \( \lambda_p = 10^{-30} \) cm² poise measured by W. K. Chan and W. W. Webb.

This large difference, expressing an easier permeation flow in our system, can explain its low effective viscosity and the facility to orient samples. While a few minutes delay is sufficient between preparation and experiments in \( \text{C}_{12}\text{E}_5\cdot\text{H}_2\text{O} \) system, the quoted phospholipidic system requires annealing for three weeks before stabilization. We propose to link this difference to the presence of defects existing in our system. These defects, screw dislocations as well as pores, connect layers and promote permeation.

On a macroscopic scale, the permeation mechanism can be expressed by the following relation [22]:

\[
\dot{u} - v_z = \lambda_p G,
\]

where \( \dot{u} \) is the displacement of layers, \( v_z \) the hydrodynamic speed perpendicular to layers and \( G \) the elastic force, similar to a pressure gradient, which creates the flow.

Fig. 8. — Lattice of focal parabolae in a lamellar sample of \( \text{C}_{12}\text{E}_5\cdot\text{H}_2\text{O} \). In order to obtain a good contrast, high dilation has been imposed.
According to this scheme, $\lambda_p$ is analogous with the Darcy coefficient for a porous medium \[23\]. From this analogy, and assuming $\lambda_p$ to be proportional to $c$, the density of defects per unit surface, we deduce the dimensional relation:

$$\lambda_p = c \frac{a^4}{\mu}$$

where $a$ is a molecular dimension (for example the radius of the core of screw dislocation, say 3 nm) and $\mu$ a viscosity.

If $c = 10^9$ defects/cm$^2$ \[10\] and $\mu = 0.1$ poise, we obtain $\lambda_p = 10^{-16}$ cm$^2$/poise.

This value is not too different from that we measured, considering the simplicity of our model, and is still much larger than that found in reference \[4\] for a « supposed » lamellar phase. This analysis suggests that this sort of defect plays an important role in permeation process and in a more general way, in transport phenomena. However, the mobility of dislocation increases with temperature (see Fig. 7), but as we do not know the behaviour of viscosity with temperature, we cannot test whether $\lambda_p$ increases like the concentration of defects, $c$.

6. Conclusion.

Compressibility modulus, $B$, in C$_{12}$E$_4$-H$_2$O lamellar phase is equal to $2.5 \times 10^7$ dyn/cm$^2$. This is a common value for smectic liquid crystals.

Splay modulus, $K_s$, is equal to $6 \times 10^{-8}$ dyn. This value is smaller than that usually assumed ($10^{-6}$ dyn) for thermotropic smectics and for lipidic bilayers; but it is consistent with a value obtained recently from ESR experiments on the same system as we studied ($K_s = 2 \times 10^{-7}$ dyn) \[24\]. Such a high flexibility is consistent with the existence of highly curved defects as revealed by ESR and electron microscopy experiments.

Compression relaxation curves appear not to be affected by these defects. Relaxation time varies as $1/\alpha$ as if the only mobile dislocations were those belonging to the grain boundary in the middle of the sample. We think that this is due to the small size of the loops, as compared with the amplitude of deformation. Under small deformations, the loops just bend but cannot act as sources of edge dislocations.

On the other hand, the mobility of edge dislocations belonging to the grain boundary is much larger ($m = 6 \times 10^{-7}$ cm$^2$ s$^{-1}$) than that measured in a phospholipidic system. We attribute this large difference to the screw component of the dislocation loop which cross layers and to any connecting defect (such as pores) which hugely promote permeation process and, as a consequence, promote the climb of mobile dislocation.

We lack quantitative data to make comparisons. Light scattering experiments, transport phenomena experiments, such as resistivity measurements, diffusion coefficient measurements, would give useful information.

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Appendix.

Rôle of screw dislocations and dislocation loops in plastic deformation. — The relaxation time, as measured on compression curves, does not vary much with the amplitude of deformation, except for a slight decrease for large amplitudes. However, we did not observe a decrease by successive jumps, as was noticed in a thermotropic smectic \[24\]. This phenomenon had been explained by a helical instability of long screw dislocations, equivalent to successive removal of layers, i.e. equivalent to the formation of edge dislocation loops. The ingoing force due to the line tension which is opposed to the growing of the instability is proportional to $1/h^2$, where $h$ is the length of the screw line, (in this case $h$ is the thickness of the sample).

« Infinite » screw dislocations exist in our sample \[10\] and they may undergo the instability. But actually we did not work in the same experimental conditions as those reported in \[25\] :

(i) The thickness of our sample is $100$ μm instead of $400$ μm. The ingoing force on a $100$ μm long screw is $16$ times larger than a $400$ μm long one. This can impeach the instability from developing.

(ii) For technical reasons (presence of the elastic tightening seal) the angle between the slides of our sample is, for the best value, $5 \times 10^{-4}$ rd. instead of $10^{-4}$. This is, in our opinion, the main reason for the non-observation of the instability: the density of edge dislocations belonging to the boundary is larger in our samples and hides the contribution of « infinite » screws.

Electron microscopy has shown that most screw dislocations were not isolated but belonged to dislocation loops which cross layers. These screws are much smaller than those which we discussed in the previous paragraph. So for reason (i) they cannot take part to plastic deformation.

We shall now discuss the contribution of the edge component of loops. Actually what are the requirements for such an edge dislocation to be active? Let $l$ be the length of the edge line, and let us assume that anchoring points on the screw lines are fixed.
Fig. 9. — Micrographs of freeze fractured samples of C₁₂E₅ lamellar phase. Samples were quenched immediately after brutal crush between two copper plates. One can see here two examples of edge dislocations, anchored on screw dislocations, and completely bent to release compressive stress. Arrows show the points where screw dislocations emerge. On micrograph 9a anchoring points lay in the fracture surface while on figure 9b the anchoring points lay a few layers under the surface of the micrograph. This is shown by the difference of contrast between the fracture steps issued from the screw dislocation and the edge dislocation.

Such a piece of dislocation, undergoing a stress perpendicular to layers will bend (Fig. 9) but it will act as a Bardeen-Herring source [26] only if the stress is bigger than the critical value given by:

\[ \sigma = \frac{2T}{bl} \]

where \( T \) is the line tension. If we take:

\[ T = 10^{-7} \text{ dyn} \]

and

\[ l = 0.5 \mu m \] [10]

it yields \( \sigma = 10^4 \text{ dyn/cm}^2 \).

Such a stress is equivalent to a compression \( a₀ \) equal to 20 layers, which is larger than we performed (\( a₀ < 10 \) layers).

So, to a first approximation, dislocation loops revealed by microscopy must not be counted as mobile dislocations. However, even if not mobile or able to act as edge dislocation sources for small deformations, these loops, as well as isolated « infinite » screws, must certainly bend and be responsible of the slight decrease of relaxation times for the highest deformations imposed to our samples.

References